TECHNICAL REPORT
NATICK/TR-07/020

AD____________________

PLASMA-ARC DEPOSITED ELEMENTAL BORON FILM FOR USE AS A DURABLE NONSTICK COATING

PHASE I

by
C. Christopher Klepper

HY-Tech Research Corporation
Radford, VA 24141

September 2007

Final Report
February 2002 – August 2002

Approved for public release; distribution is unlimited

Prepared for
U.S. Army Natick Soldier Research, Development and Engineering Center (NSRDEC) Natick, Massachusetts 01760-5018

DISCLAIMERS

The findings contained in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

DESTRUCTION NOTICE

For Classified Documents:

Follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For Unclassified/Limited Distribution Documents:

Destroy by any method that prevents disclosure of contents or reconstruction of the document.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
07-09-2007	Final	4 February 2002 – 2 August 2002

4. TITLE AND SUBTITLE
PLASMA-ARC DEPOSITED ELEMENTAL BORON FILM FOR USE AS A DURABLE NONSTICK COATING - PHASE I

5a. CONTRACT NUMBER
DAAD16-02-C-0024

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
C. Christopher Klepper

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
HY-Tech Research Corporation
104 Centre Court
Radford, VA 24141

8. PERFORMING ORGANIZATION REPORT NUMBER
D0154

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Natick Soldier Research, Development and Engineering Center (NSRDEC)
Attn: AMSRD-NSC-CF-E (C. Haering)
Natick, MA 01760-5018

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
NATICK/TR-07/020

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Report developed under Small Business Innovation Research Contract. Under this Phase I SBIR contract, HY-Tech Research performed development of an abrasion resistant, non-stick coating for cookware used by the U.S. Army in the field. The deposition technique uses a vacuum arc source of elemental boron, a high-temperature material with excellent hardness, lubricity and chemical inertness. HY-Tech's boron arc source is based on the vacuum (cathodic) arc process, which produces the coating material by very efficient evaporation of the solid cathode. The Phase I project demonstrated that it is possible to deposit adherent coatings of amorphous boron on aluminum alloy substrates, even at high deposition rates (>1nm/s) and on surfaces that are not highly polished. The Phase I project successfully developed a deposition procedure for adhering boron to non-polished 3004Al samples, as cut from a commercial roaster pan by varying the substrate bias program as well as substrate preparation. Microscopy indicated good adhesion to the substrate; however, tests in a high-salt environment led to delamination, suggesting that chemical bonding is weak or non-existent, which is consistent with our predictions.

15. SUBJECT TERMS

ALUMINUM	SANITATION	PLASMAS(PHYSICS)	PLASMA TRANSFER ARC	COOKING DEVICES
ABRASION	SBIR REPORTS	NONSTICK COATINGS	PLASMA ARC DEPOSITION	KITCHEN EQUIPMENT
COATINGS	FOOD SERVICE	PROTECTIVE COATINGS	FIELD COOKWARE	
BORON	PLASMA ARCS	MAGNETIC PROPERTIES	FILTERED VACUUM CATHODIC ARC	

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Chad Haering
U	U	U	U	27	**19b. TELEPHONE NUMBER** *(Include area code)* (508) 233-6040

THIS PAGE INSERTED FOR FORMATTING PUPOSES

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PREFACE

This report documents the progress of a project to develop a durable non-stick coating for Army cookware. The approach was to apply an elemental boron coating to an aluminum substrate using plasma arc deposition.

This work was performed between February 2002 and August 2002 under Small Business Innovation Research Contract number DAAD16-02-C-0024 by HY-Tech Research Corporation of Radford, Virginia. This information could not be disclosed outside the Government for a period of five years from the completion of the work. This period ended August 2007.

PLASMA-ARC DEPOSITED ELEMENTAL BORON FILM FOR USE AS A DURABLE NONSTICK COATING - PHASE I

1. PROJECT SUMMARY

This SBIR program is concerned with the development of an abrasion resistant, non-stick coating for cookware used by the U.S. Army in the field. The deposition technique uses a vacuum arc source of elemental boron, a high-temperature material with excellent hardness, lubricity and chemical inertness. This unique source has been developed by HY-Tech Research Corporation under previous SBIR funding from the Department of Energy and the National Science Foundation. [1] The technical objective of the Phase I effort was to demonstrate adherent, pure boron coatings on aluminum alloys used in field cookware. The coatings would be deposited by the arc source process and the properties specified in the Phase I solicitation (low friction, high hardness, low abrasion, resistance to salt-corrosion) would be demonstrated. The development of an effective magnetic ducting system, which would filter out *macroparticles* (particle debris from the cathode) and expand the boron plasma to produce a uniform, debris-free coating over large areas, was left for a Phase II project to be proposed as a follow-on program. The hope was to demonstrate the coating's properties in spite of the macroparticles and then benefit from Phase II funding to include effective filtering as a part of the scale-up of the process.

HY-Tech's boron arc source is based on the *vacuum (cathodic) arc process*, which produces the coating material by very efficient evaporation of the solid cathode. [2,3] The key in its development was primarily a powder consolidation technique to produce boron cathodes, which can sustain the high stresses induced by the arc discharge. Effective heating was also necessary to get boron, a semiconductor at room temperature, to conduct the arc current. In addition to the high rate of material production, vacuum arc deposition also benefits from the fact that the output vapor is in a fully ionized state. This allows for good control of the energies of deposition and, as a result, of the adhesion to the substrate and of the density of the film. Previous funding had allowed HY-Tech to demonstrate that its boron coatings can be made to adhere to various substrate materials. However, there had been little opportunity for optimization of the coatings and extensive evaluation of their properties and limits.

This SBIR project is gave HY-Tech a first opportunity, since the development of this coater, to test and optimize its unique deposition source for boron, for a specific commercial application. Specifically this application called for non-stick coatings to be used on aluminum cookware, used by the U.S. Army in the field. The desired properties are a high hardness, low abrasion, low friction, and a high resistance to corrosion due to salt and food acids. The idea is to have cookware that can be easily scraped clean, with minimal use of water, minimizing water consumption and transportation in the field, while maintaining sanitary standards. Boron appeared to be ideal for this application. Being naturally very hard (~30GPa), it was expected to resist abrasion from cleaning pads and metal cookware. In fact, since it is more than twice as hard as sand, it was thought that sand could be used for scraping the cookware, if that was the only abrasive material in the battlefield!

This project also gave HY-Tech an opportunity to further explore the limitations of coating aluminum alloys with boron. That the arc-deposited boron adhered to aluminum was one of the surprises of the Phase II NSF project. Thermodynamic calculations have indicated a repulsive interaction between these elements, and HY-Tech is still promoting boron as an ideal coating to protect dies used in molten aluminum alloy die-casting (partly because the aluminum will not solder to the die). It would appear that the fully ionized state of the boron vapor generated by the arc allows, by judicious use of electrical biasing of the substrate, for sufficient interlayer mixing to get, at least, good mechanical bonding.

Indeed, the Phase I project successfully developed a deposition recipe for adhering boron to non-polished 3004Al samples, as cut from a commercial roaster pan. An optimal recipe was found by varying deposition parameters, such as the substrate bias program, as well as substrate preparation. Microscopy on these coatings, with and without diamond-tip scratching, indicated good adhesion to the substrate. However, tests in a high-salt environment (salt-fog or brine) led to delamination (without actually salt-pitting either the substrate or the film that floats off!). This suggests that chemical bonding is weak or non-existent, which is consistent with our predictions. Unfortunately, it also suggests that the absence of chemical bonding adversely affects the ability of this coating solution to resist salt-corrosion (and, presumably, food acid corrosion). This in turn suggests the necessity of an intermediate layer, which will facilitate the chemical bonding, while preserving the desired properties of boron as the hard coating and the aluminum as the substrate.

Because the deposition is based on a vacuum arc discharge, *macroparticles* (debris from the boron cathode) also get incorporated into the film. [4-6] These microscopic boron particles can be harder than the film. They can scratch the film and interfere with wear studies. They can also leave pinholes, which encourage corrosion. This significantly limited HY-Tech's ability to demonstrate all the predicted propertied of the boron coating for this application. However, some of the properties were shown, in spite of the macroparticles. For coatings put down with the optimal recipe, hardness in excess of 20GPa (twice as hard as silicon) was measured. It was shown that the coatings have sufficiently low friction and resistance to thermal cycling, as well as resistance to corrosion, to meet the application requirements.

It was clear from the Phase I results that a scale-up of the present coater must be able to predictably expand the boron plasma plume to uniformly coat a typical flat griddle or frying pan used by the Army and to filter out all the macroparticles. This can be done by a magnetic duct system, properly designed to match the boron arc source. As a part of the Phase II proposal effort, HY-Tech opened a dialogue with Fraunhofer, USA (Plymouth, Michigan), which has extensive experience with vacuum arc technology in commercial scale and design capability for magnetic ducts. This is the U.S. branch of the German Fraunhofer Organization, a non-profit organization, whose charter is to bridge the gap between innovative research and commercial production. It was determined that Fraunhofer would be an optimal strategic partner to HY-Tech in this area. HY-Tech would not only benefit from technology transfer of proven magnetic duct (and other vacuum arc) technologies, but also from the links that Fraunhofer has to potential customers for HY-Tech's boron coating technology.

It is expected that the market for boron coatings on aluminum alloys will also extend beyond cookware, both for military and civilian applications. For example, this coating would be ideal for automotive components that are exposed to both salt-corrosion and severe abrasion from sand. There is an effort to convert an increasing number of automotive components (for both civilian and military use) to aluminum, to reduce weight and fuel consumption. Exhaust and suspension components, most susceptible to these corrosive and abrasive elements are also considered for conversion. The proposed Phase II project, which was planned to address scale-up of the process and macroparticle removal, was not approved for funding. However, it is believed that this Phase I project produced valuable information on the properties of boron coatings on aluminum alloys. The results of this work can now be used to set the stage for future development, which can benefit, if not directly the funding agency, one or more defense agencies in dual-use applications, such as the ones just mentioned.

2. RESULTS OF THE PHASE I WORK

The Phase I project demonstrated that it is possible to deposit adherent coatings of amorphous boron on aluminum alloy substrates, even at high deposition rates (>1nm/s) and on surfaces that are not highly polished. At least two recipes for specifically coating 3004Al samples from actual commercial cookware were developed. In fact, in the early stages of the project, the substrate material presented the most serious challenge. Bulk 3004Al is impossible to purchase in small quantities (i.e. less that several tons). On the other hand, actual cookware (such as roasting pans) do not have particularly smooth surfaces, such as we have dealt with in past deposition studies. In addition, as we found out, the surfaces of such cookware exhibit a very thick oxide layer, a part of which is actually worked into the aluminum subsurface by the extrusion process. The development of our new recipes had to overcome these new and unexpected obstacles and was a result of a larger set of coating experiments than we had originally envisioned for the Phase I project.

Table 1 shows the various runs listed by the substrate we used. Table 2 shows partial results of these runs (or, at least, a description of the film obtained).

Table 1. List of substrates coated during the Phase I project.

Substrate	description of substrate	run date(s)	substr. bias	other run details
22-1	1100Al, parted, acetone-cleaned	29-Apr-02	(-500V, -100V)progr.	
33	6061 Al disk, 7cm DIA, 2mm thick, machined at HY-Tech	29-Jan-02	(-500V, -100V) progr.	
36	Mini-pan #1 6061 Al, ~5.5cm DIA, 1cm thick, w/walls ~60-degree steep	14-Feb-02	(-500V, -100V)progr.	
37	6061 Al disk, ~5.5cm DIA, 2mm thick, machined at HY-Tech	7-Mar-02	(-500V, -100V)progr.	
40-series	3004 Al disk, 2.25" dia x 0.08" thk, cut from Lincoln #5315 baking pan			
40-1		Mar&Apr-02	(-500V, -100V)progr.	
40-2		10-Apr-02	(-500V, -100V)progr.	
40-3		21-May-02	pulsed-dc @-500V	acid treat, BN/B
40-4		don't coat		
40-5		don't coat		
40-6		21-May-02	pulsed-dc @-200V	acid treat, BN/B
40-7		22-May-02	pulsed-dc @-200V	acid treat, BN/B
40-8		23-May-02	pulsed-dc @-200V	acid treat, BN/B
40-9		27-30 May-02	pulsed-dc @-200V	acid treat, BN/B/BN
40-10		31-May-02	pulsed-dc @-200V	acid trt, run in Ar
40-11		31-May-02	pulsed-dc @-200V	acid trt, run in N2
41-series	3004 Al disk, 1" dia x 0.08" thk, cut from Lincoln #5315 baking pan			
41-1		24&29-Apr02	fixed at -500V	pt clean btw runs
41-2		30-Apr-02	fixed at -500V	substr @30+4cm
41-3		1-May-02	fixed at -500V	first with BN interlr
41-4	(set near source to collect macros)			
41-5	(set near source to collect macros)			
41-6		6&9-May-02	pulsed-dc @-500V	w/BN interlayer
41-7		10&14-May02	pulsed-dc @-500V	1st acid treated
41-8		14-May-02	pulsed-dc @-500V	acid treated, B only
41-9		15&16-May-02	pulsed-dc @-500V	like 41-7

Table 2. Rough description of the film obtained on each of the substrates in Table 1. Partial analysis results mentioned. More details in the text.

Substrate	description of film	Plans for film analysis	analysis results
22-1	Thick, focused, few bad spots		
33	Whitish (~4cm) with blue halo	RBS; done; Salt-pit next	B uniform, but Cu up to 40% in cntr
36		RBS; done; Salt-pit next	B uniform, but Cu up to 40% in cntr
37		Use for macropt cleaning tests	
40-series			
40-1	Some rings; a bit of delam later on	RBS; done; Salt-pit next	Pure B (tiny amount of Mo)
40-2	Some rings; off-center;no delam	RBS; done; Salt-pit next	Pure B (tiny amount of Mo)
40-3	No delam;no arc damage;non-uniform	to MicroPhotonics for friction	
40-4	no coating	Salt-pit	
40-5	no coating	Salt-pit	
40-6	Very thin looking (bluish) film		
40-7	No delam;no arc damage;non-uniform	Cooking tests	mixed results from cooking
40-8	No delam;no arc damage;non-uniform	to MicroPhotonics for friction	
40-9	small grains in BN top layer		mixed results from cooking
40-10	Very thin looking (bluish) film		
40-11	unstable film		
41-series			
41-1	Dark B film, but flaking off		
41-2	Small warmtracks; more uniform		
41-3	Uniform blue; some arc damg nr cntr	RBS	Only 50nm
41-4			
41-5			
41-6	Dark B coat, but delam throughout		
41-7	Brown central region, green around it!	sent to Taber on 16-may-02	scrapes-off due to macroparticles
41-8	Purple center, ~green around	sent to Taber on 16-may-02	scrapes-off due to macroparticles
41-9	Dark brown center, light brn around	to JW for Hardness/Friction	Only 100nm

Our film deposition was also affected by the fact that a significant upgrade to our boron source coincided with the start of the Phase I project. In this upgrade, we replaced the original source assembly by one that could handle very long-pulse operation, by including water-cooling in the anode and the structures that surround the heated cathode. A large part of the design of the new source was technology transferred from the Lawrence Berkeley National Laboratory (LBNL) with which we had a past collaboration on a Department of Energy (DOE) Small Business Technology Transfer (STTR) project. The design included a copper (actually a copper-tungsten alloy) anode, which would be used in place of our originally pure tungsten anode.

Unfortunately, this latter aspect of the new source did not work as expected. Initial coatings were found to contain copper. The water-cooling did not prevent evaporation of anode material. We have not been able to determine yet if this LBNL design used elsewhere with metal cathodes also leads to copper contamination. It is possible, however, that the anode operates very differently in a metal vacuum arc than in a non-metal, like boron, which is much harder to evaporate.

This latter complication forced us back to an operation with a non-cooled, tungsten anode and limited the duration of our deposition pulses. Then, the number of (1-2.5s long) pulses was limited by the lifetime of the trigger, which requires frequent maintenance. This, in turn, impacted our ability to produce thick coatings. In spite of this, our project was very successful and productive. All good coatings were characterized at the Surface Modification and Characterization (SMAC) facility of the Oak Ridge National Laboratory (ORNL). There, Jim Williams, our materials consultant is an authorized user of the 2.4MeV He^{++} Rutherford Backscattering Spectroscopy (RBS) system, which has high sensitivity for boron. RBS studies showed that the W anode allowed again for high purity, and therefore, hard boron. Figure 1 shows the analysis of a nanoindentation measurement (also at SMAC) on one of our sample (40-2) and at 3 different locations.

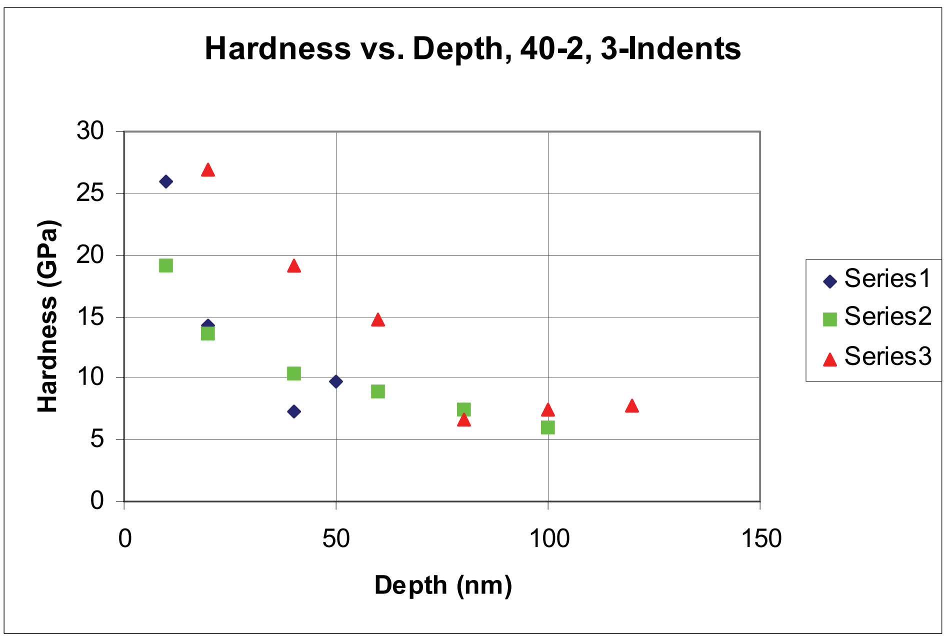

Figure 1. Processed nanoindentation data at three locations on sample 40-2 indicating a hardness in the range of 20-27GPa (at least twice the hardness of Si). The rapid drop in the apparent hardness with depth is a result of the very thin film on a very soft substrate. This also contributes to the large scatter in the data. The surface roughness (due to the macroparticles) also contributes to this scatter (roughness however can only lower the apparent hardness; cannot raise it!)

On the basis of past nanoindentation measurements on thicker coatings and on harder substrates, we expect that thicker coatings on aluminum alloys will measure 26GPa or higher. So this result is clearly consistent with our expectations. Abrasion resistance was harder to measure. We sent two samples to Taber Industries (Buffalo, NY) for a free demo test. A 500-cycle test with a No. 17 wearaser head on a linear abrader took both the thin film and part of the substrate with it. Then, we accepted an offer from Taber for a more delicate test (less cycles, more inspections) it was quickly determined that it was the macroparticles that were removing the film. Some of the macros that we were not able to wash off the substrate were dragged off by the wearaser and acted as a grinding compound with properties quite similar to diamond particles. Other macroparticles remained attached (probably melted into the substrate). These actually abraded away the wearaser! We note that the solid boron particles are much harder than anything in the wearaser. In addition, they are also harder than the film. Pure boron has a hardness of 30GPa. Clearly, macroparticles are a bigger issue than anticipated in the Phase I write-up. This is why we made the elimination of the macros such a major thrust in the work plan of our Phase II proposal.

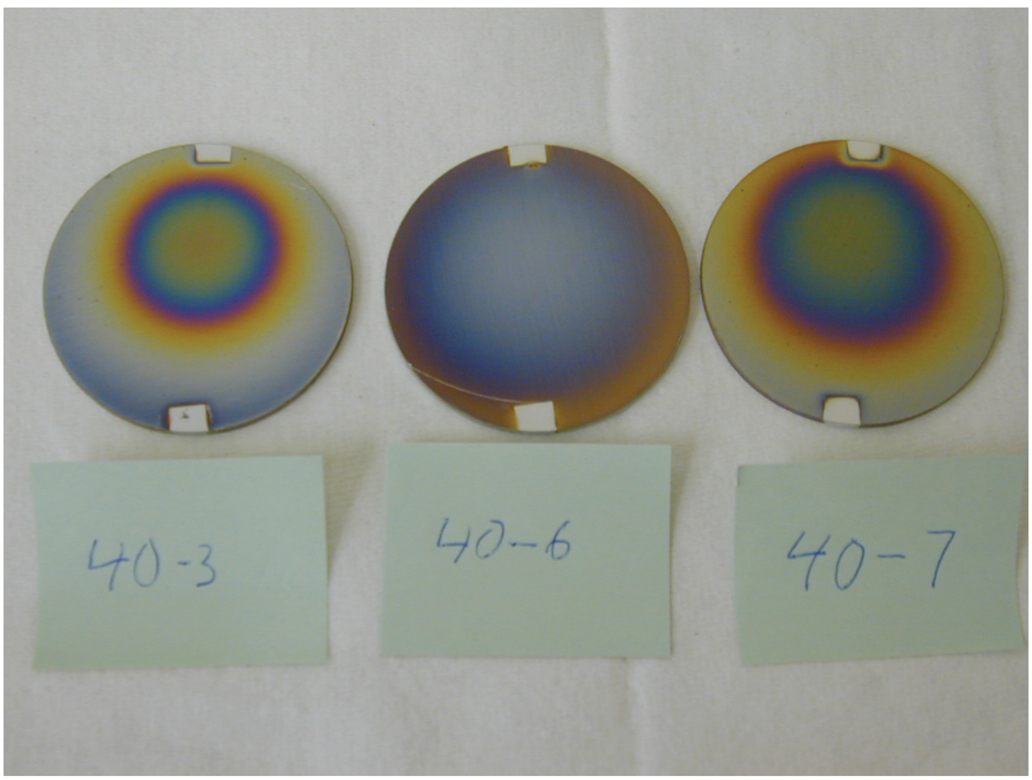

Figure 2. Three of the best adherent, arc-damage free coatings on large samples (40-series) of 3004 Al (cut from a commercial roasting pan).

Figure 2 shows a set of coated samples obtained with our optimized recipe for best adhesion to these 3004Al substrates (without non-boron interlayer). The changes in color are optical effects due to the thinness of the films and correspond to changes in the thickness, which decreases radially out. The difference in uniformity and radial extent between samples is due to a small change in the position of one of the magnetic field coils that go around the vacuum arc chamber. The configuration of the anode of the source and the gap between the anode and cathode also affect the uniformity. Optimization of the expansion and uniformity of the plume are important issues of scale-up for this process. This is where a strategic alliance, like the one we had proposed with the Fraunhofer organization, would greatly expedite progress toward a commercial coater, since they have the capability to design optimal magnetic filters for plume filtering, expansion and homogenization, using proprietary computer design codes.

As mentioned, the films appeared adhere adequately to the substrate, especially once an optimal recipe was determined for this particular substrate material and surface. This recipe involved acid cleaning of the substrate to remove the thick oxide. The oxide of aluminum is a very good electrical insulator. This can lead to charge build up on the surface, since the insulator prevents current to flow through the substrate as the bias voltage is applied. In turn, the charge build-up can lead to micro-arcs on the surface that can damage the coating. The recipe also used nitrogen in the discharge for the first two pulses to form a BN interlayer (a better match of thermal expansion coefficient of the substrate). To further reduce the possibility of charge build-up (since boron is also a poor conductor, especially in thick layers) a bias program that included positive going pulses at a 50kHz rate actively neutralized any charge buildup on the substrate. (This was originally motivated by arcing between large substrates and the nearby chamber walls; but it turned out to help much beyond this problem). A scratch-test image of an optimal recipe B coating on 3004Al is shown in Fig. 3.

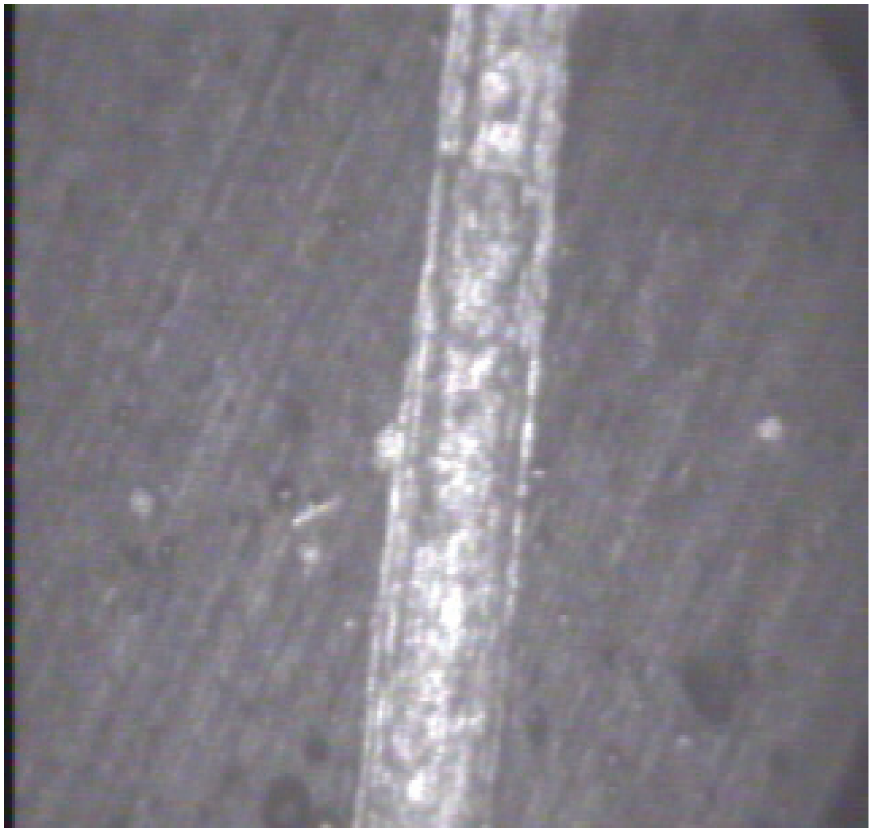

Figure 3. A diamond tip scratch test on sample 40-9 showing the excellent adhesion of the boron coatings on 3004Al commercial pan substrates with the optimized recipe.

Since thermal cycling is an issue for this application, we took one of the sample (40-9), heated it in a conventional oven to 500°F for about 0.5 hours. Then, we dropped it directly into cold water (from the tap). Under the microscope, we observed <u>no degradation in the film</u>.

The Phase I plan also called for actual cooking tests on our best samples. There was concern, however, that the very small thickness of these coatings would put them at a disadvantage (recall that these are very thin, very hard coatings on a very soft substrate!). However, with the Phase II proposal deadline approaching, it was decided to attempt some rudimentary cooking tests anyway. The results were mixed, but encouraging. Before attempting to cook on our film, we invested on a high quality commercial non-stick pan (a T-Fal™ griddle). We tried frying an egg without first priming the surface with oil or similar lubricant. This does not work too well, though ultimately the egg comes off with a tough, dry texture. Lubricating another part of the pan with some butter (which we had available instead of oil) we got a better result. Thus, we took this approach on the first test on our boron coating. We heated sample #40-7 on a large (spiral) burner on a standard kitchen electric stove, set to medium heat. With the butter nearly burning off, we dropped a small quantity of pre-beaten eggs. It cooked rapidly and could be easily removed with a plastic spatula. The surface cleaned off easily with dish soap and water. As we felt the surface by hand during washing, we could feel the roughness of the surface due to the macroparticles! (In past project, our handling of the few good coatings on various substrates was much more delicate. This project provided opportunity for subjecting our coatings to much more handling and a significantly larger range of testing).

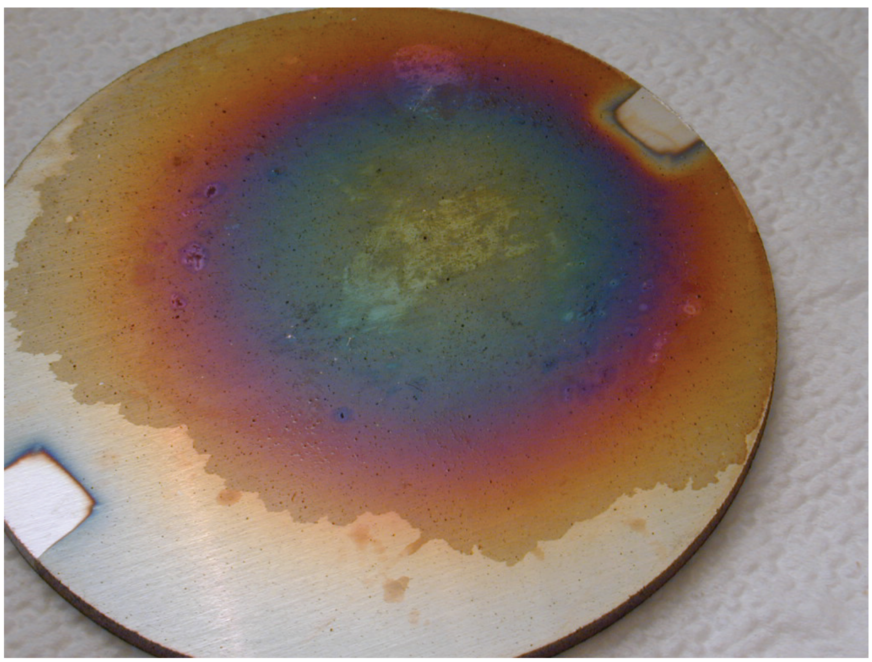

Figure 4. Coated sample 40-7 after cooking egg on butter and then cleaning with dish soap and water using only dish cloth. The light discoloration in the central region, where the egg was cooked may just be an optical effect (films are very thin).

Figure 4 shows an image of the film after the egg test and subsequent cleaning. The film appears intact. The change in the color is not understood, but would likely not be there if the coating was much thicker (then, all these optical effects would vanish).

We then cooked a small piece of a cheese enchilada on the same sample. Before the cheese began to burn, it could be easily lifted off the surface. However, when it burned, it left a black residue, which could not be lifted off with a plastic spatula. Cleaning with a ScotchBright™ scrubbing pad removed a great deal of the residue, but still left a black stain. Interestingly, the thin boron film survived all this cleaning action. This is exciting for us. Again, this is the first project that has allowed us to put our coatings to such severe testing. (Later on, after the Phase II proposal, we did some RBS testing of the black stain. It was determined that the boron did not react with the carbon and that the boron coating was still intact under the carbon. This again is a very positive result!)

It should be recalled at this point that PTFE-based coatings did not become as good as they are now over a brief period of time. Early versions did not do as well with their non-stick aspects, especially without some oil. They also stained easily. These days, after three decades of research and development, they are highly optimized. PTFE is only one ingredient. Some have even bits of mica imbedded to give added hardness to the surface. In this project, we have the very first evaluation of using a hard, metallurgical coating, as a non-stick coating. What would make its non-stick property better is not obvious and will require further research. However, the fact that the film, even in this very thin form, does not come right off after cooking and thermal cycling is a very encouraging result!

We actually did a second set of cooking tests on sample 40-9, which looked a lot like sample 40-7 on a macroscopic scale. However, we had attempted to add a thin layer of boron nitride to the surface of this new sample. The idea was to improve the non-stick property by two means: (a) to passivate the surface (perhaps better than the natural oxide in regards to preventing reaction with the carbon in the food) and (b) to provide an actual boron nitride coating, which may itself be less reactive (since a reaction with the carbon was still suspected). However, at least in this one test (we repeated cooking of a piece of cheese enchilada) we did not find the sample to act any better than the pure boron coating.

In this second sample we used more intense cleaning to try to remove the black residue. This included the use of sodium bicarbonate with the ScotchBright™ pad and even some bleach (full strength). The boron film remained intact. By the end, the black residue only remained in the boundary of the burned region. It is interesting to point out that the ScotchBright™ pad cleaning avoids macroparticle effects by removing them without pressing them against the film (only on one or two occasions did we see a scratch due to a macroparticle in this cleaning process.

It was clear by the time that we considered testing for friction against stainless steel that the macroparticles would also adversely affect the measurements. However, we sent two samples to Micro Photonics in Irvine, CA, for the measurement of the coefficients of static and kinetic friction. Since the ASTM standard test in the solicitation is for a polymer film and, in any case, it was not available from Micro Photonics, we also sent two samples cut out from the T-Fal™ griddle. The results of these friction tests on sample 40-3 compared to the commercial PTFE sample are shown in Tables 3 and 4.

Table 3. Dynamic Coefficient of Friction (Sample 40-3)

	Average μ Run 1	Average μ Run 2	Average μ	Std dev
T-Fal	0.042	0.035	0.039	0.003
40-3	0.263	0.250	0.257	0.005

Table 4. Static Coefficient of Friction (maximum value taken at beginning of curve)

	μ Run 1	μ Run 2	Average μ	Std dev
T-Fal	0.116	0.058	0.087	0.024
40-3	0.364	0.225	0.295	0.057

Considering the large effect that the surface roughness can have on this measurement, we find these results very encouraging. We believe that without the macroparticles, we can easily get to average friction values significantly below 0.2. To further substantiate this we show a plot of the actual measurement of friction versus position on this same sample, as received from Micro

Photonics (Fig. 5). Here, the bumps due to the macroparticles are clearly seen. We also see a clear lower limit that would correspond to a smooth surface.

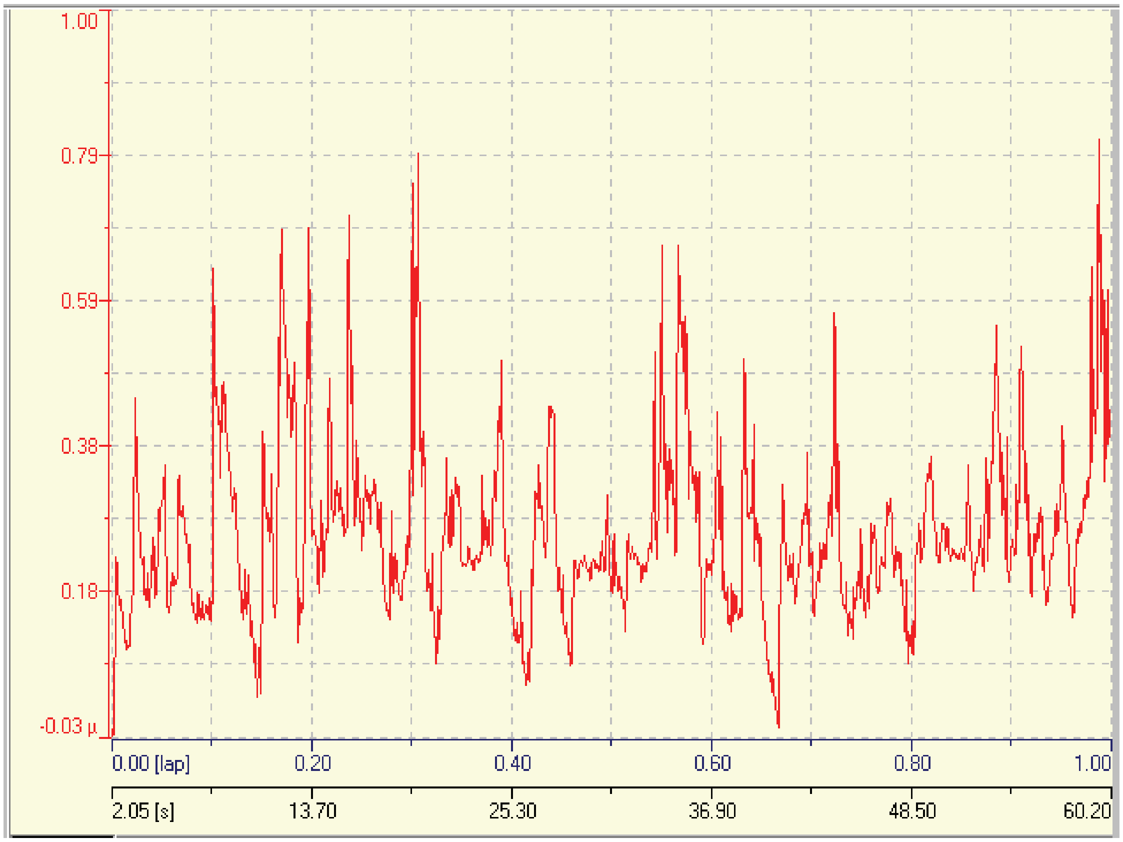

Figure 5. Friction as a function of time (or lap) on sample #40-3 showing large variations due to the macroparticles (graph taken from the report sent to us by Micro Photonics, Irvine, CA).

We qualify here the above statements on the friction measurement by indicating that the measurement had to be somewhat customized due to the delicate nature of a thin film on a soft substrate, as well as to the severe abrasion that actual stainless steel would face from the hard boron macroparticles. As a result, Micro Photonics used a 6mm alumina oxide ball with a 0.5N load. The measurements we carried out without lubricant, in air, at a humidity of 45-50% and at room temperature (23°C). A tangential speed of 0.06cm/s was used in a track radius of 1.25 and 3.75mm (data from the larger radius shown above).

In fact, later results by the same company and on the same sample, but using a nano-tribometer with a stainless steel stylus, gave friction coefficients about 10 times lower. However, without further study it is not certain that this was purely due to the contact material or some other instrument-related issue. It is interesting, however, since on that scale the effect of the particles can be avoided.

Finally, corrosion resistance tests were performed courtesy of Army Research Laboratory, Aberdeen Proving Ground, MD, in collaboration with Dr. J.K. Hirvonen. Samples 40-1 and 40-2 were sectored into portions for hardness tests and for corrosion tests. Corrosion tests consisting of 144 h of exposure in the salt fog test apparatus, per ASTM B-117, and of the GM 9540 to 6 cycles have been performed thus far. Tests on accompanying, as-received, 3004 alloy have been performed also. B-117 is a salt fog test at 95°F. GM 9540 consists of a cycle, which includes a gentle liquid salt spray at ambient temperature, exposure to saturated vapor at 40°C and a drying cycle at 50 % humidity and 60°C, all of which requires some hours for one cycle.

It turned out that salt pitting was hardly an issue, even for the uncoated alloy. Commercial aluminum alloys vary greatly in their resistances to salt pitting corrosion, and, apparently, 3004 may be one of the better ones. However, there was a problem with delamination of the coating for these particular samples. Almost all of the coating came off for sample 40-1 and a good fraction, perhaps half, came off for 40-2. The bare alloy became somewhat dull, but did not pit. These results seem to be broadly consistent with the hardness measurements, where it seemed possible to acquire meaningful results for 40-2, but results for 40-1 were ambiguous.

It will be noted that these two samples were ones for which no surface cleaning, acid pickling, or treatment of the "swaged in oxide layer" was done before coating. At the time of the Phase II proposal, there was reason to believe that later coatings had better adhesion. More recently, however, a quicker test was devised, based on a fully saturated salt-water solution (essentially brine). This solution was produced by Jim Williams at ORNL, to try to understand the disappointing results at ARL. He was first able to reproduce the results with some small sections of the older coating, which he had saved for such contingency. Then, when he soaked one of the "optimal recipe" coatings in the solution, he found that it also eventually came off the substrate. Again, no pitting damage is found on either substrate or floating coating.

How the salt-water contributes to the delamination of the otherwise well bonded, boron coating is only beginning to be understood. As mentioned in the introduction, our present view is that the bonding is only mechanical and not chemical. It has been forced by atomistic mixing at the interface by the energetic ions provided by the arc source in combination with the substrate bias (i.e. the arc assures that all the arriving boron atoms are ionized, so that the bias affects them all). This mechanical bonding, which overcomes the thermodynamic repulsion between boron and aluminum (also discussed in the introduction), is probably sufficient for most applications that do not involve corrosion (e.g. just for abrasion resistance).

In the late stages of the project, it was decided to try an idea to use titanium as the interlayer between boron and aluminum. Titanium is a light material that is known to adhere well to aluminum and to provide corrosion protection. It is also known to bind well with boron. Finally, it is also very easy (and therefore inexpensive) to deposit by either magnetron sputtering or vacuum arc techniques. As it turned out, a Ti-coated sample of 1100Al was available at ORNL and was sent to HY-Tech by J. Williams, who then characterized the coating, tested it in his brine solution and then forwarded it to Jim Hirvonen at ARL-Aberdeen. Before and after the brine treatment, the coating looked very good. However, after the treatment at Aberdeen, we saw pitting of the aluminum at the locations of the pores left by the macroparticles (unlike 3004Al, 1100Al pits). Still, the coating did not come off. This is considered, at this point, as a very positive finding: A thin (~50nm) coating of Ti can promote chemical bonding of the boron and increase its capability to resist a severe salt-corrosive environment.

3. ESTIMATES OF TECHNICAL FEASIBILITY

As mentioned, the goal of the Phase I was to demonstrate that the properties of vacuum arc deposited coatings on 3004Al meet the needs of this application, i.e. for a non-stick, hard, abrasion and corrosion resistant coating. The experiments were carried out on small samples of the material, which was practical for the size of the coater that was available for the project. By the time of this writing, we are aware that a Phase II project will not be awarded. However, it is worth discussing in some detail the feasibility of this coating approach at a commercial scale for actual field cookware.

The capability to adhere boron coatings to this aluminum alloy has clearly been demonstrated. The problems caused by the oxides and the uneven surface morphology due to the extrusion process have been overcome by acid pickling of the substrate and pulse-dc bias techniques. The lack of chemical bonding has been overcome by a thin Ti interlayer. None of these added process steps is expected to substantially increase the cost of commercially processing the cookware. Acid treatment is very common before thin film deposition. Usually, in vacuum coating techniques, it is followed by glow discharge cleaning, a step that was not necessary in our process. The pulse-dc operation was standard in the commercial power supplies we were already using for biasing the substrate. Finally, titanium sputters very easily and is one of the most common materials used as cathodes in commercial vacuum arcs. Therefore, either a Ti sputter cathode or a Ti arc-source can be easily added within the same deposition chamber to get the thin interlayer before the boron.

This leaves *plume management*, i.e. controllable expansion and/or steering of the boron plasma plume and the related removal of the macroparticles (cathode debris) as the only significant challenge in commercial scale-up. As was extensively discussed in the Phase II proposal, the macroparticles (typically solid boron chunks in the 1-10μm range) are either solidly incorporated into the film or come off the film leaving behind pores, through which corrosion of the substrate can occur. The macroparticles also roughen the surface, reducing the coefficient of friction. If loosely bound, they can also contribute to abrasion of the film as they are dragged across the surface by the abrader. In any case, however, macroparticles are a common problem with vacuum arc deposition. Technologies already exist for plume management both in the form of techniques and in the form of computer models to optimize these techniques to a specific vacuum arc source. The approach we had proposed for our Phase II project would have included an alliance with an organization that had both the experience and the needed technology to design an optical filter for our boron arc source.

Finally, we discuss non-stick issues. The only proven non-stick coatings in today’s market are polymer (specifically PTFE) based. The present R&D program is trying to break new ground by adapting a metallurgical coating to non-stick cookware. The emphasis was in the adherence of the coating to aluminum, for which there was prior evidence, as well as the hardness and corrosion resistance. Optimizing non-stick aspects was not a focus in Phase I. However, the literature on boron-based films suggests that, when heated in ambient air, these coatings will generate a lubricious acid (boric acid) and this will make the coating self-lubricating. There was a reasonable expectation, as a result of this literature, that the food will not stick. It is obvious in the description of the Phase I results that the simple tests on very thin boron film was not conclusive. It pointed to potential problems with our assumptions and it is clearly worth exploring further.

Assuming, however, the worse possible conclusion, i.e. that in general the boride generation property of the film is not useful as a non-stick property when it comes to food, then there are possible solutions that include additional coating layers. One such solution is presented here[1]. Suppose that a very thin layer of a non-stick polymer was deposited on top of the boron coating. If the layer is much thinner than any envisioned contact, the utensil will not be able to dig into the polymer to initiate any damage. The underlying boron layer will be harder than the utensil, which is likely to be a metal (e.g. stainless-steel). A further benefit of this approach is that the polymer will fill in the pores in the coating (assuming particles were not filtered, but just scraped –off, leaving pores in their place).

A further idea for improvement of the surface of the coating is to intentionally incorporate (or leave in the existing) boron macroparticles in the boron coating and then top it with the thin polymer layer in such a way that most large particles poke through the layer. This may further reduce wear of the top layer, since a relatively large contact area utensil, such a spatula, will mostly ride over the macroparticles, avoiding the polymer layer. In fact, as it turns out, a similar approach is taken by manufacturers of high-grade PTFE-based, non-stick pans. For instance, they use mica particles embedded into the PTFE coating to achieve the same effect.

One of the key points illustrated by the last two paragraphs is that a complex surface engineering problem, which requires a combination of numerous mechanical properties, is bound to have a complex coating solution. In turn, a complex coating solution has to be developed in a sequence of R&D activities. The Phase I project was the first step, which showed that boron can be made to adhere to the aluminum alloy and can potentially serve as one of the very important components of this coating solution. The evaluation of the proposed non-stick top-layer approach would have to be the focus of a very similar R&D project (or sub-project).

[1] It is acknowledged that this idea is actually based on a suggestion made to the author by Larry E. Seitzman of Caterpillar, Inc., Peoria, IL

4. CONCLUSIONS

Here a list of the conclusions drawn in the various sections of the report is provided:

- Vacuum arc deposited boron coatings can be made to mechanically adhere to 3004Al sample, as cut from commercial cookware, with the proper combination of substrate cleaning and electrical bias programming.
- Such mechanically bonded films do not maintain their adhesion in a salt-corrosive environment. Preliminary data indicate that this limitation may be overcome with a thin titanium interlayer.
- The coatings maintain their high hardness, even on the soft aluminum substrate.
- The macroparticles prevent successful demonstration of the predicted wear resistance and the resulting surface roughness affects friction measurements. Still, friction measurements strongly suggest sufficiently low friction.
- Cooking tests of the boron film had mixed results, suggesting that a top layer may be needed as a part of the solution. Thus a possible "system solution" may be 3004Al-sputtered Ti – vacuum arc deposited BN – vacuum arc deposited B – thin polymer (possibly with embedded macroparticles to further reduce wear, as discussed).
- The project not only allowed for the development of one component of a promising non-stick cookware solution for severe environments, but also gave HY-Tech Research an opportunity to study the properties of its unique coating as deposited on aluminum alloys. What has been learned may be used to open opportunities for commercial use of the coating in a broad range of applications involving surface engineering of aluminum components.

5. REFERENCES

1. C.C. Klepper, J.M. Williams, R.C. Hazelton, E.J. Yadlowsky, et al. "Amorphous Boron Coatings Produced via Vacuum Arc Deposition Technology." Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, Volume 20, Issue 3 (May 2002) pp. 725-732.

2. Handbook of Vacuum Arc Science and Technology: Fundamentals and Applications, P.J. Martin, D.M. Sanders, R.L. Boxman, editors, Noyes Publications, Park Ridge, NJ, U.S.A., 1995.

3. Ian G. Brown, "Cathodic Arc Deposition of Films," Annu. Rev. Mater. Sci., 28, pp. 243-69, 1998.

4. R. L. Boxman and S. Goldsmith, "Macroparticle contamination in cathodic arc coatings: generation, transport and control," Surface and & Coatings Technology, 52, pp. 39-50, 1992.

5. T. Schuelke, and A. Anders., "Velocity distribution of carbon macroparticles generated by pulsed vacuum arcs," Plasma Sources Sci. Technol., 8, pp. 567-571, 1999.

6. A. Anders, "Approaches to rid cathodic arc plasmas of macro and nanoparticles: A Review," The 26th International Conference on Metallurgical Coatings and Thin Films, April 1999.